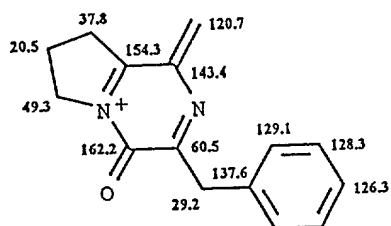


^{13}C NMR data



^1H NMR data

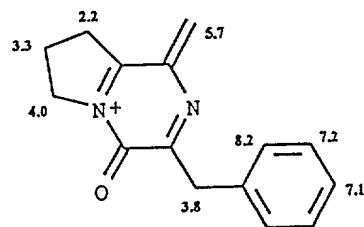


Figure 1: Structural formula of the product of the intramolecular cyclisation of H-Phe-Pro-pyridinium methyl ketone. The characteristic chemical displacements (in ppm) determined by means of ^{13}C NMR and ^1H NMR are assigned to the corresponding atoms.

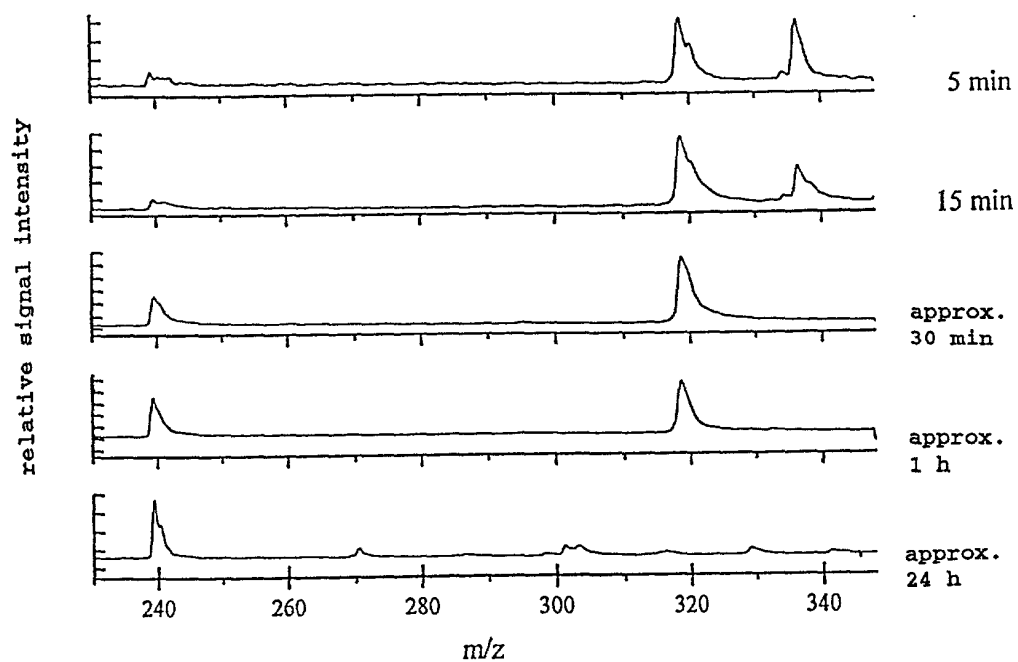


Figure 2: MALDI-TOF mass spectra of the cyclisation of H-Phe-Pro-pyridinium methyl ketone in an aqueous buffer solution pH = 7.6, recorded according to the incubation period.

5

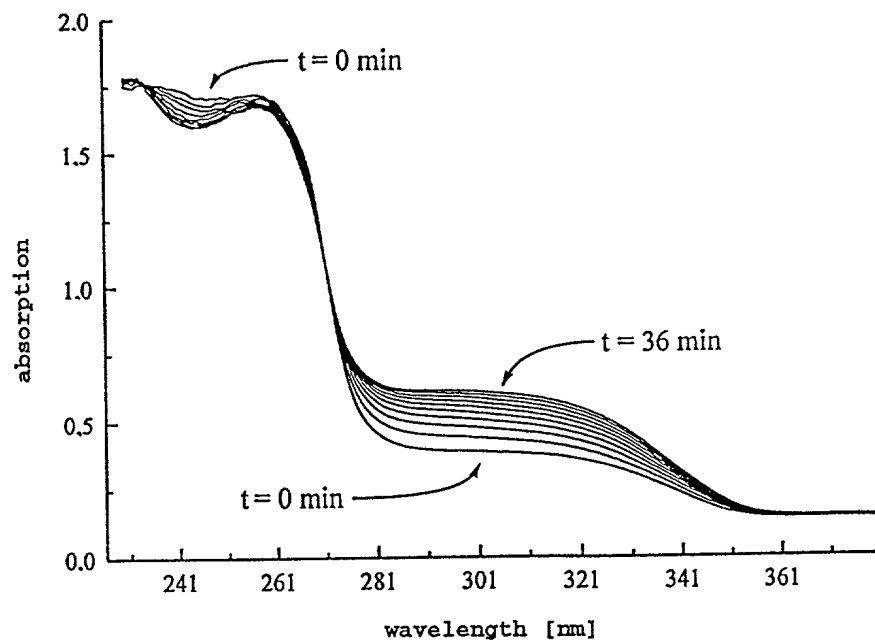


Figure 4: UV spectra of an aqueous solution of H-Phe-Pro-pyridinium methyl ketone incubated in 0.1M HEPES buffer, pH = 7.6, at 30°C. The cyclisation reaction was monitored over a period of 40 minutes.

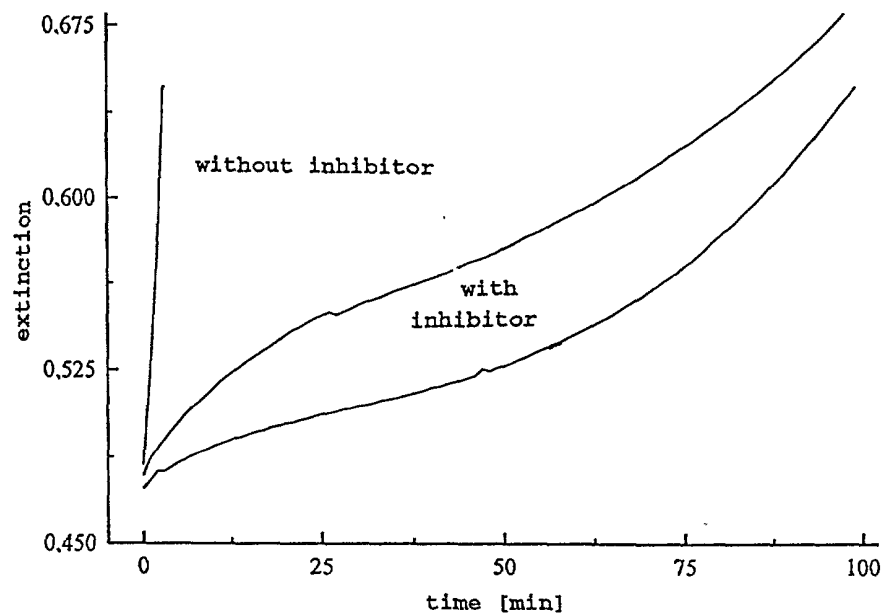


Figure 5: Progress curves of the DP IV-catalysed hydrolysis of the substrate H-Gly-Pro-pNA in the presence of $2.8 \times 10^{-3} \text{ M}$ H-Val-Pro-pyridinium methyl ketone, $0.06 \text{ } \mu\text{g/ml}$ of DP IV, $4 \times 10^{-4} \text{ M}$ H-Gly-Pro-pNA in the batch, 0.1 M HEPES buffer, $\text{pH} = 7.6$, 30°C .

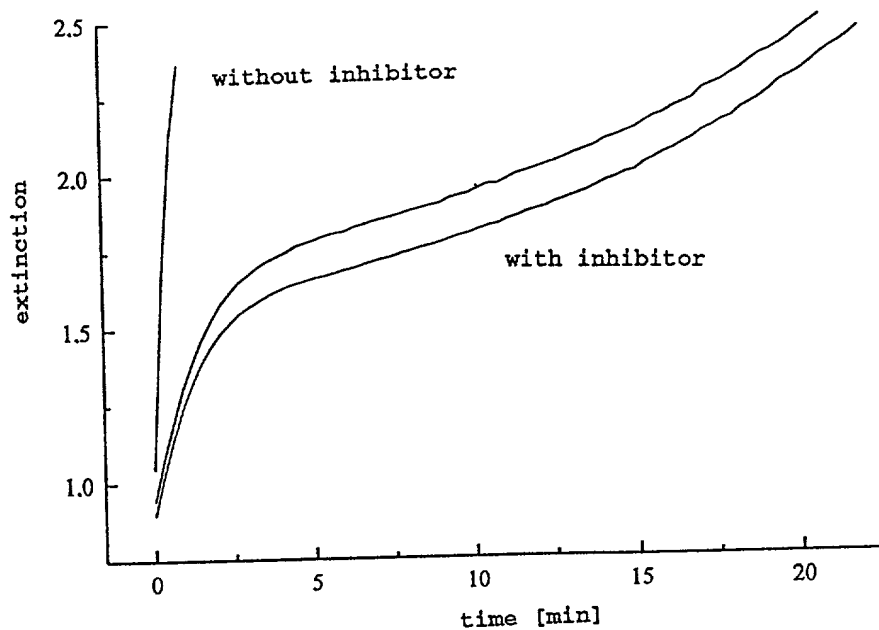


Figure 6: Progress curves of the DP IV-catalysed hydrolysis of H-Gly-Pro-pNA in the presence of 2.1×10^{-4} M H-Phe-Pro-pyridinium methyl ketone, 0.06 $\mu\text{g/ml}$ of DP IV, 1.0×10^{-3} mol/litre of H-Gly-Pro-pNA in the batch, 0.1M HEPES buffer, pH = 7.6, 30°C.

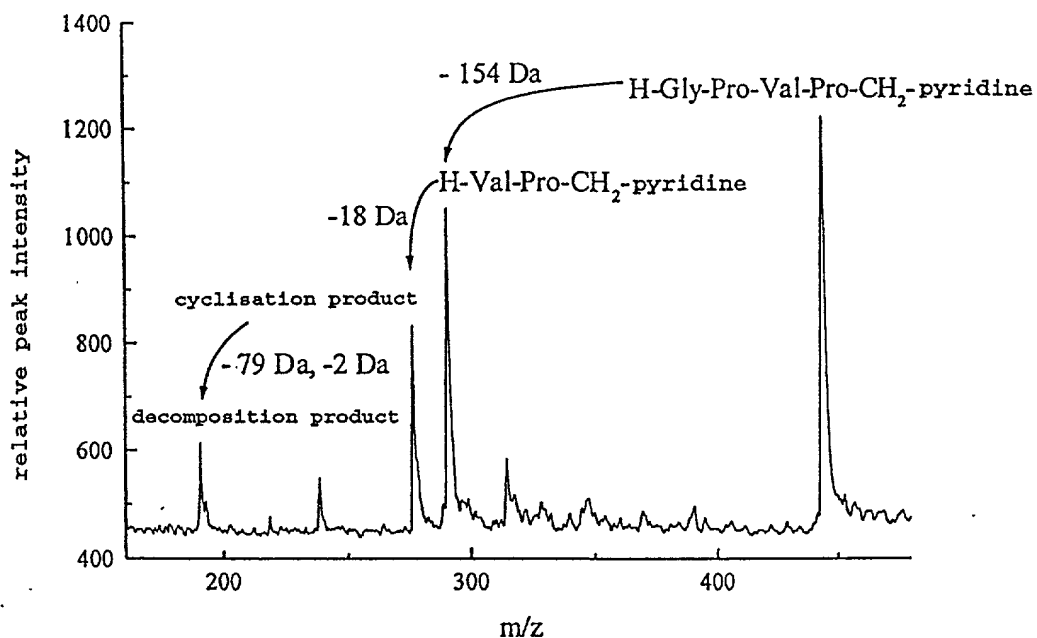


Figure 7: MALDI-TOF mass spectrum of the incubation batch of the DP IV-catalysed hydrolysis of H-Gly-Pro-pNA in the presence of 2.6×10^{-5} mol/litre of H-Gly-Pro-Val-Pro-pyridinium methyl ketone, 0.06 $\mu\text{g/ml}$ of DP IV, 2.0×10^{-4} mol/litre of H-Gly-Pro-pNA, 0.1M HEPES buffer, pH = 7.6, 30°C. Recorded after an incubation period of 60 minutes.

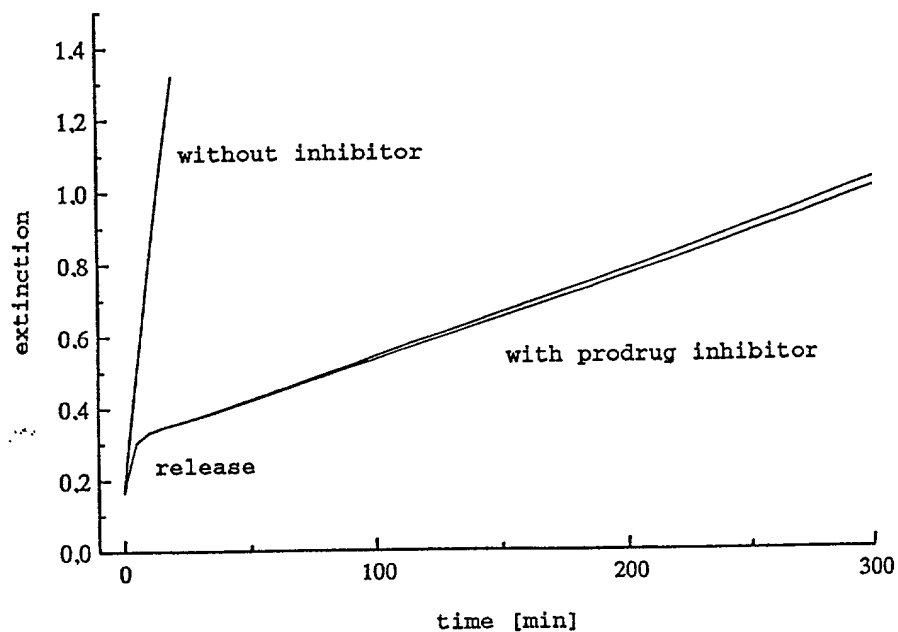


Figure 8: Progress curves of the DP IV-catalysed hydrolysis of H-Gly-Pro-pNA in the presence of 2.6×10^{-5} mol/litre of H-Gly-Pro-Val-Pro-pyridinium methyl ketone, 0.06 $\mu\text{g/ml}$ of DP IV, 2.0×10^{-4} mol/litre of H-Gly-Pro-pNA in the batch, 0.1M HEPES buffer, pH = 7.6, 30°C.